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Aluminum gallium nitride (AlGa<sub>N</sub>) has long been recognized as a promising radiation hard optoelectronic material. AlGa<sub>N</sub> has a wide direct band gap and therefore has potential applications in the fabrication of short wave-length devices, e.g., detectors and light-emitting diodes in the visible to ultraviolet region and its piezoelectric properties and high acoustic velocities make it attractive for acoustic devices. The technical objective in Phase I was to determine if low temperature sources based on covalently bonded Group III-nitrogen compounds could be used to prepare AlGa<sub>N</sub> films by gas source molecular beam epitaxy. The program required to investigate low temperature AlGa<sub>N</sub> source materials was separated into two parts, (1) the synthesis, purification, and pyrolysis of gallium-nitrogen adducts and aluminum-nitrogen adducts and (2) the growth of Ga<sub>N</sub> by chemical beam epitaxy. We clearly demonstrated under CBE conditions Ga<sub>N</sub><sub>x</sub>Cy films could be grown using compounds with preexisting Ga-N bonds whereas no films were formed using trimethylgallium. Dimethylgallium amide was shown to produce dramatically lower carbon content films in the presence ammonia than did trimethylgallium in the presence of ammonia.

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# FINAL REPORT

## "Gas Source Molecular Beam Epitaxial Growth of GaN"

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# FINAL REPORT

## "Gas Source Molecular Beam Epitaxial Growth of GaN"

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## a. INTRODUCTION AND TASK OBJECTIVES

Aluminum gallium nitride (AlGa<sub>N</sub>) has long been recognized as a promising radiation hard optoelectronic material. AlGa<sub>N</sub> has a wide direct band gap and therefore has potential applications in the fabrication of short wave-length devices, e.g., detectors and light-emitting diodes in the visible to ultraviolet region. Its piezoelectric properties and high acoustic velocities make it attractive for acoustic devices.

It has proved difficult to grow electronic quality epitaxial films of AlGa<sub>N</sub>. Problems are encountered with the inadequate purity of the nitrogen source and with the high temperatures required for its decomposition. The high process temperatures necessary often render AlGa<sub>N</sub> use incompatible with optoelectronic device fabrication processes and lead to quality problems caused by nitrogen vacancies.

Although theoretical evaluations of AlGa<sub>N</sub> clearly indicate its promise, its potential has never been adequately investigated because of the poor and irreproducible quality of the films that are being grown today. Efficient, pure, low temperature sources for the gas source molecular beam epitaxial (GSMBE) growth of aluminum gallium nitride will essentially introduce a *new* semiconducting material for evaluation.

The technical objective in Phase I was to determine if low temperature sources based on covalently bonded Group III-nitrogen compounds could be used to prepare AlGa<sub>N</sub> films by GSMBE. The program required to investigate low temperature AlGa<sub>N</sub> source materials was separated into two parts, (1) the synthesis, purification, and pyrolysis of gallium-nitrogen adducts and aluminum-nitrogen adducts and (2) the growth of Ga<sub>N</sub> by GSMBE.

We proposed to investigate the pyrolysis of the Group III-nitrogen source compounds with the goal of developing an understanding of their decomposition pathways and how they relate to effective GSMBE growth. The films grown using these test compounds were to be examined for growth rate, surface morphology, and carrier concentration and mobility. The relationship between Ga<sub>N</sub> growth kinetics and layer characteristics and the decomposition pathways would be evaluated to provide the foundation for a rational theory of AlGa<sub>N</sub> source design.

In summary, the questions we asked were:

- If gallium-nitrogen and aluminum-nitrogen adduct compounds are synthesized, can they be used to deposit high quality epitaxial AlGa<sub>N</sub> layers in an GSMBE reactor?
- Are the candidate source reagents sufficiently volatile to permit gas-phase transport to the reactor?
- Do the candidate source reagents decompose in the reactor to deposit only AlGa<sub>N</sub> at the desired growth temperature? Co-deposition of impurity elements, e.g. carbon, may occur.

This requirement is often the most difficult to satisfy. Even minor decomposition pathways can produce intermediates that are sufficiently reactive with the surface to contribute unwanted atoms.

- Are the source reagents pure? Two types of purity are required. First, the compound must be of high chemical purity to insure that the vapor pressure of the reagent remains constant during sample use. Second, the samples must be of high elemental purity to ensure that extrinsic impurities are not introduced into the GSMBE-grown layers. The choice of synthetic and purification methods is critical in insuring the high elemental purity.

In Phase I the objective was to demonstrate that more efficient precursors to aluminum gallium nitride could be developed and to establish baseline GSMBE materials quality. It was not anticipated that electronic-grade films would be grown during Phase I. During a Phase II, optimized and purer sources could become available, optimized GSMBE growth parameters could be developed, and consequently high quality films would result.

## b. BACKGROUND AND TECHNICAL PROBLEMS

The preparation of AlGaN at low temperature by MOVPE has been frustrated by a lack of suitable nitrogen sources. The high temperatures required to decompose ammonia ( $\text{NH}_3$ ) and the presence of oxygen-containing impurities in the reaction gases are believed to cause nitrogen vacancies and n-type donor impurity centers.

GaN, AlN, and AlGaN have been grown by vapor phase epitaxy using both halide and organometallic precursors to Al and Ga. Ammonia has been the preferred source of nitrogen, although isolated reports describe the use of trifluoroamine,<sup>1</sup> hydrazine,<sup>2,3</sup> triethylamine,<sup>4</sup> and even plasma-excited nitrogen.<sup>5</sup> Typically temperatures in excess of 800°C and high  $\text{NH}_3$  flow rates have been required to achieve moderate growth rates of epitaxial material. Problems have been encountered because high temperature growth causes nitrogen vacancies and the purity of the source reagents is inadequate (the nitrogen source is the most suspect). The purity problem is undoubtedly exacerbated by the low growth rates and the large excess of ammonia that is required.

The reason for the high temperature requirement for the growth of AlGaN by currently used methods is found in the high nitrogen-hydrogen bond strength. Table 1 displays the bond energies relevant to the production of AlGaN. Methane and arsine are included for comparison.

TABLE 1. Bond Dissociation Energies<sup>6</sup>

		<u>kcal/mole</u>
Methane	$\text{CH}_3\text{-H}$	104
Ammonia	$\text{NH}_2\text{-H}$	103
Trimethylgallium	$(\text{CH}_3)_2\text{Ga-CH}_3$	77
Arsine	$\text{AsH}_2\text{-H}$	61
Trimethylaluminum	$(\text{CH}_3)_2\text{Al-CH}_3$	45

Product catalysis of the decomposition of arsine and trimethylgallium has been shown to reduce the temperature required for gallium arsenide (GaAs) formation,<sup>7</sup> but the strength of the N-H bond is so high that even catalyzed growth of GaN is slow at 800°C. There is little interaction between the gallium alkyl and ammonia in the gas phase, and surface catalysis of ammonia decomposition is insufficient to lower the pyrolysis temperature below 800°C.

We proposed to use source reagent compounds containing both gallium and nitrogen, with nitrogen bonded to carbon, in the hope of providing a lower energy decomposition pathway.

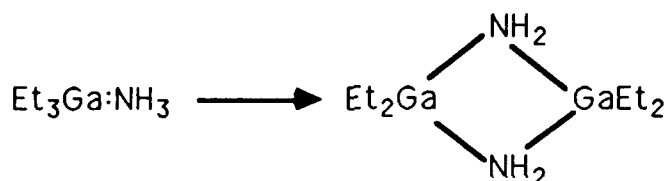
The technical objective in Phase I was to determine if low temperature sources based on covalently bonded Group III-nitrogen compounds could be used to prepare AlGaN films by GSMBE. The program required to investigate low temperature AlGaN source materials was separated into two parts, (1) the synthesis, purification, and pyrolysis of gallium-nitrogen adducts and aluminum-nitrogen adducts and (2) the growth of GaN and AlN by GSMBE.

### c. TECHNICAL APPROACH

Compounds that contain both the Group III and the Group V atom could offer outstanding stoichiometric control during AlGaIn preparation, if compounds with the appropriate vapor pressures and decomposition pathways were identified. Three sets of compounds that may meet these criteria for gallium-containing source reagents — azidoalkylgallium adducts, trialkylgallium-ammonia complexes, and trialkylgallium-hydrazine adducts — have been conceived. Analogous compounds exist for the aluminum-containing source reagents. Some of these compounds have been described in the chemical literature, and others would be synthesized for the first time. Stoichiometric gallium-nitrogen and aluminum-nitrogen compounds rather than an excess of nitrogen source might be capable of depositing device-quality epitaxial AlGaIn layers.

#### Gallium-Nitrogen Source Reagents

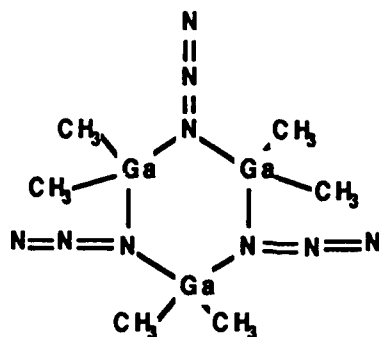
The prospect of pre-forming a gallium-nitrogen bond in the source material is an attractive option that was first recognized by Andrews and Littlejohn in 1975.<sup>8</sup> They used the adduct formed from triethylgallium and ammonia which underwent decomposition to give the dimeric amide.



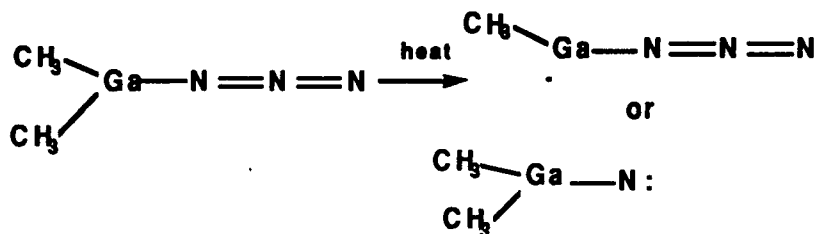
This material decomposed further upon standing in the bubbler to give an unidentified viscous material. However, GaN could be grown in a crude reactor using no external source of N. The temperatures used ranged from 600-1000°C and the mobilities were low (~30 cm<sup>2</sup>/V·s), but the carrier concentrations ranged as low as 5 x 10<sup>14</sup> cm<sup>-3</sup>. These results are encouraging; further refinements in source design and preparation are likely to result in the development of an "adduct" system that will yield epitaxial GaN of high quality.

There are three classes of gallium-nitrogen compounds that potentially could be used in the growth of AlGaIn: alkylgalliums and gallium hydride complexes or reaction products with (1) hydrazoic acid and its derivatives, (2) ammonia and amines, or (3) hydrazine and its derivatives.

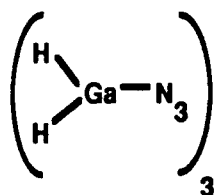
**Hydrazoic Acid Derivatives.** Azidodimethylgallium and azidodiethylgallium are trimeric solids with low vapor pressures.<sup>9</sup> The thermal decomposition of these compounds has not been reported and should be investigated.



Upon heating in the gas phase, dissociation will probably occur to yield monomers.

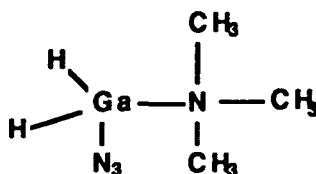


It is possible to envision two distinct routes for decomposition of the monomer, loss of methyl or of nitrogen. If decomposition of the azo moiety precedes loss of the methyl group, either methyl migration or C-H insertion could lead to intermediates that would ultimately contribute to carbon incorporation in the gallium nitride film. To avoid these possibilities, azidodihydrogallium could be used.

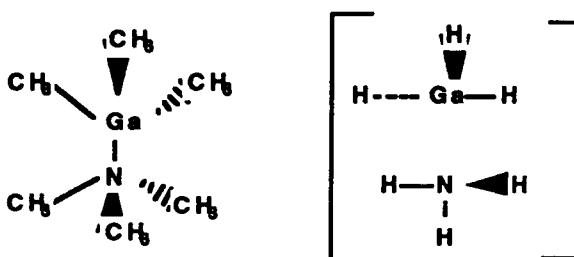


It is difficult to predict the degree of association, although coordination with an amine could produce a monomeric form.

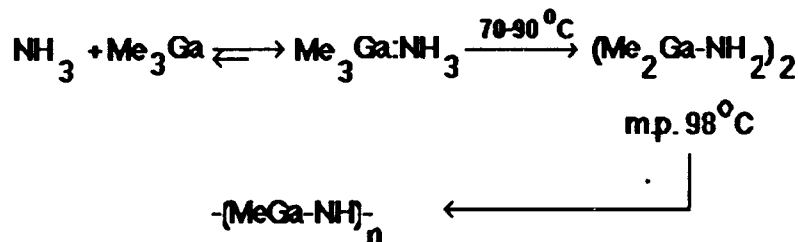




**Ammonia Derivatives.** A wide variety of derivatives of gallium and ammonia are known, ranging from the stable trimethylgallium-trimethylamine<sup>10</sup> to trihydrogallium-ammonia which rapidly loses two moles of hydrogen at room temperature to form a polymer.<sup>11</sup>

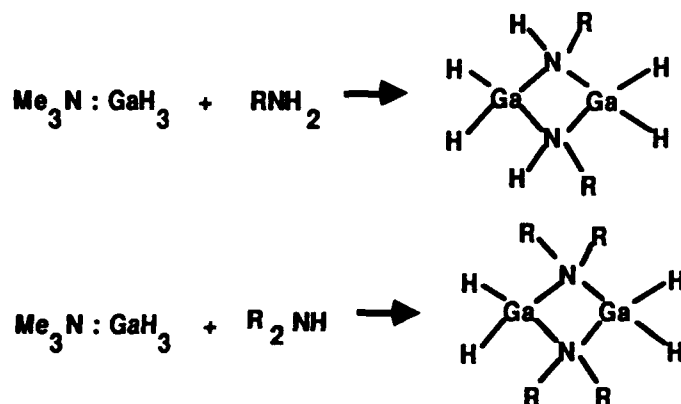


We have focussed on two types. The first comprises compounds formed from trialkylgalliums and ammonia. Coates found that trimethylgallium and ammonia formed a complex ( $\Delta H_f$  measured at 18 kcal/mole<sup>12</sup>) that lost methane at 70-90°C to form a dimer.<sup>13</sup> The dimer was stable to 140°C.



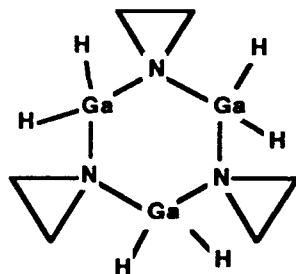
Andrews has described the successful use of the analogous diethylgallium amide to grow GaN. His choice of the ethyl derivative centered on his preference for a liquid rather than a solid in the bubbler. However, this material decomposed upon standing at room temperature to yield an unidentified viscous solid. Such difficulties relating to the stability of the source reagent would be less likely to occur in the methyl case.

The second type of compound that deserves attention is a series of complexes formed from gallane and primary or secondary amines.<sup>11,14,15</sup>

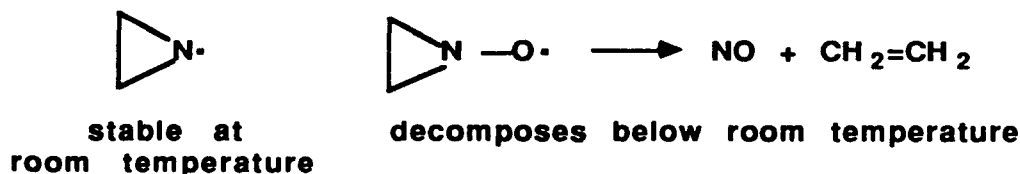


R = Me, Et, iPr, Bu

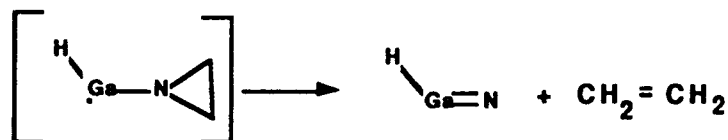
The complexes formed where R= Me or Et are involatile because they are highly associated. As the size of alkyl group increases the degree of association decreases and the volatility increases. This is fortunate, since the isopropyl-N bond and t-butyl-N bond are likely to be weaker than the corresponding methyl or ethyl nitrogen bonds. The most attractive of the adducts formed from secondary amines is the compound derived from ethyleneimine (aziridine).<sup>16</sup>



Although aziridine itself is an unlikely nitrogen source because of its tendency to isomerize upon pyrolysis, prior complexation with gallium could introduce new decomposition pathways. For example, the aziridiny radical is stable at room temperature, whereas the nitroxide is too unstable even to be observed at low temperatures.<sup>17</sup>

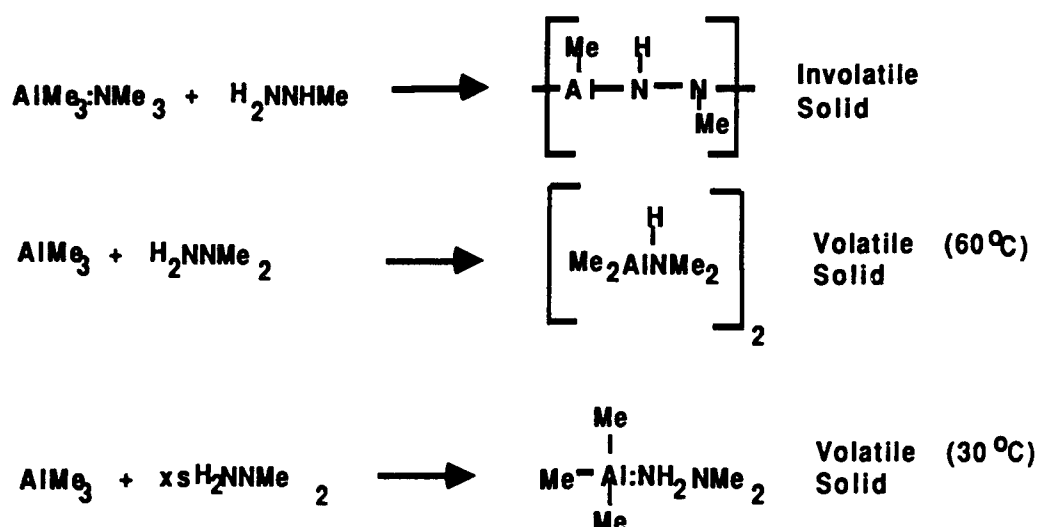


We believe that upon pyrolysis of the aziridine-gallane adduct, a gallium hydrogen bond will be broken and that rapid loss of ethylene will occur in a manner analogous to the aziridine nitroxide example above.



Carbon contamination is less likely to occur in the pyrolysis of the adducts in general, because it is thermodynamically more favorable to produce gallium nitride rather than multiply bonded carbon-nitrogen species.

**Hydrazine Derivatives.** This aspect of gallium-nitrogen chemistry has been the least studied. Several aluminum compounds have been reported; some are polymeric crystalline solids, others volatile solids.<sup>18</sup>



Synthesis of the gallium derivatives should be straightforward, but predictions of their physical properties or their decomposition pathways are merely speculative and should be delayed pending experimental verification.

### Aluminum-Nitrogen Source Reagents

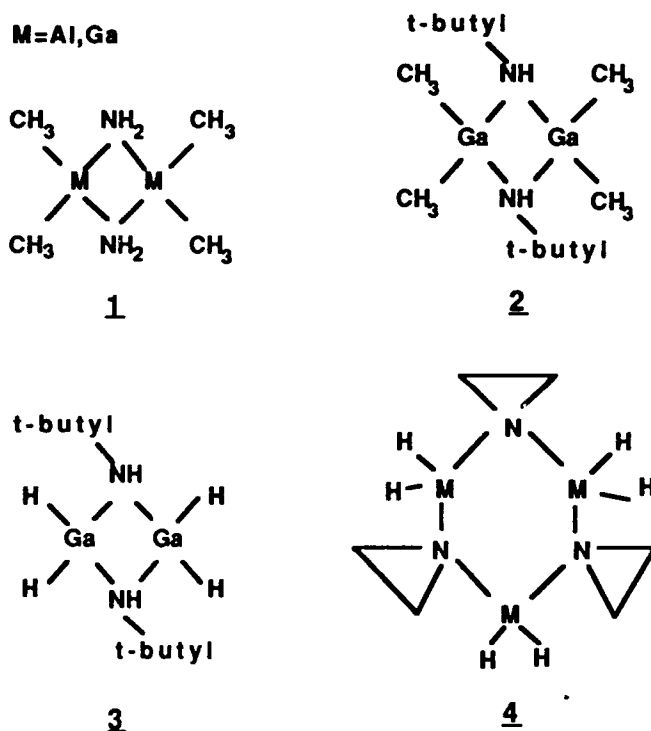
The synthesis of the aluminum compounds and their use in film growth is expected to be analogous to the synthesis and use of the gallium compounds. Many of the analogous aluminum amine, azide, and hydrazine adducts and compounds have been synthesized, but not for use in the electronics industry.

Carbon incorporation in AlGaAs layers has been a significant problem because of the high reactivity of Al atoms and the strength of the aluminum carbon bond. Carbon incorporation is likewise expected to cause problems in AlGaN. In the selection of the aluminum reagent it is important to keep this mind. Aluminum hydride complexes or aluminum alkyls that can decompose by beta-hydride elimination lessen the possibility of carbon incorporation.

### Reagent Synthesis and Characterization

For each potential source reagent, fundamental research on synthesis, purification, and mechanism of decomposition must be linked to film growth studies, which provide feedback to the design and synthesis work as well as the purification effort. Synthesis of new compounds for low temperature deposition represented Phase I of this project. Once the organometallic precursors were synthesized, they were tested for AlGa<sub>2</sub>N deposition.

In Phase I we concentrated on known compounds so that the premise that stoichiometric compounds could yield low temperature growth of AlGa<sub>2</sub>N could be tested as quickly as possible. The compounds originally included in the initial phase are shown below.



We discovered that the literature syntheses of compounds 3 – 4 could not be reproduced in our laboratories. Instead of abandoning the film growth efforts, we prepared the series of Ga and Al compounds **1**. Unfortunately, the presence of Ga-C and Al-C bonds in the precursors **1-Ga** and **1-Al** increased the likelihood that carbon would be incorporated into the film in contrast to compounds 3-4 which contain only Ga-H bonds.



**1-Ga**



**1-Al**

AlN films growths were attempted in a low pressure CVD apparatus but no evidence for film growth was obtained.

Finally, the growth of GaN was attempted in a chemical beam epitaxy apparatus using 1-Ga with and without  $\text{NH}_3$ . Auger analysis showed that films grown in the presence of ammonia contained significantly lower concentrations of C than those grown in the absence of ammonia. Preforming the Ga-N bond in the starting material is also important – films grown using trimethylgallium and ammonia showed little nitrogen and significant amounts of carbon.

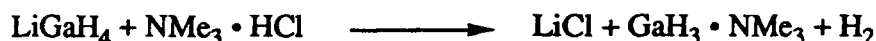
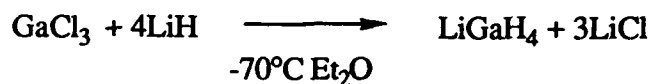
## d. PHASE I TECHNICAL RESULTS

The experimental work was divided into two phases, reagent synthesis and film growth studies.

### d.1 REAGENT SYNTHESIS

NMR spectra are taken in  $C_6D_6$  unless otherwise noted.

#### Trimethylamine gallane



The preparation of gallium hydride-trimethylamine is a two step process. The unstable intermediate, lithium gallium hydride, must be prepared just prior to use to minimize decomposition. The details of handling gallium trichloride are not often found in the literature so we share some of our experiences.

Gallium chloride is extremely hygroscopic and corrosive. It is commercially supplied (Aesar) in sealed glass ampoules. We found that the best way to handle this material is to melt the solid into one chunk in the ampoule using a heat gun (be sure to open ampoule first under  $N_2$ , then use septa or rubber tubing connected to  $N_2$  bubbler to maintain inert atmosphere). The ampoule containing a single solid mass of  $GaCl_3$  is then taken into the glove box, smashed, (use parafilm wrap on ampoule to minimize fragmentation), and the glass fragments plucked away from the virgin solid  $GaCl_3$ .

The chunks of gallium chloride may be further pulverized using a mortar and pestle and subsequently stored in glass bottles with poly or teflon lined caps. Rubber septa caps will be attacked by  $GaCl_3$ .

A solution of gallium chloride in ether was prepared by direct addition of solid  $GaCl_3$  (using a flexible Teflon solids transfer tube) to 800 ml of ether in a three neck, one liter flask under nitrogen with stirring. The ether solution was cooled using an ice bath, and the other necks were sealed with septa; one neck was used as an  $N_2$  bubbler inlet, the other was used for a thermocouple probe.  $GaCl_3$  was added in portions over 1.5 hours, and the temperature was maintained at  $2-5^\circ C$ .

A 2 liter three neck flask equipped with a mechanical stirrer was charged with lithium hydride (LiH) (33.6 g, 4.2 mol, weighed in an argon-filled glove bag). The other necks were sealed with septa, again for a nitrogen bubbler inlet/outlet and thermocouple probe insert. Ether was added (500 ml) by cannula transfer to the flask to make a slurry. The LiH slurry was cooled using dry ice/isopropanol. When the temperature was below  $-60^{\circ}\text{C}$ , the  $\text{GaCl}_3$  solution was added using an 18 narrow gauge cannula. Addition was complete in 1.5 hours without incident, and the temperature remained below  $-58^{\circ}\text{C}$ .

The initial grey LiH slurry was gradually replaced by a white suspension of LiCl and  $\text{LiGaH}_4$  in ether. The reaction mixture was then allowed to warm to  $\sim 0^{\circ}\text{C}$ . (If the temperature was allowed to rise above  $0^{\circ}\text{C}$ , thermal decomposition occurred producing hydrogen gas, lithium hydride, and gallium metal.)

Trimethylamine-hydrochloride (67 g, 0.7 mol) was then loaded into a solids addition tube, custom made by gluing a 60 ml polypropylene bottle to the end of a ground glass jointed (24/40 male) glass tube. The trimethylamine-hydrochloride was weighed out and loaded into this tube inside a nitrogen filled glove bag. This tube was connected to a teflon flex tube connector (Aldrich) with a 24/40 male joint on one end and a 24/40 female joint on the other. By use of this flex tube adapter, the solids transfer tube was connected to the reaction flask.

The  $\text{LiGaH}_4$ -containing reaction mixture was cooled below  $-50^{\circ}\text{C}$  using dry ice/isopropanol, and the trimethylamine-HCl was added in portions to the stirred suspension. Total addition time was 1 hour, 15 minutes. The temperature remained a fairly steady  $-60^{\circ}\text{C}$ . A continuous, but slight,  $\text{H}_2$  evolution was observed out the bubbler at this low temperature, but not enough to account for all of the hydrogen that should have been produced by the reaction.

The white suspension was allowed to warm slowly. Gas evolution became quite vigorous between  $-45$  and  $-35^{\circ}\text{C}$ , then subsided somewhat as the reaction warmed to  $0^{\circ}\text{C}$ . However, gas evolution continued for several hours after the solution warmed to  $0^{\circ}\text{C}$ . Attempts to warm the suspension to ambient temperature were scrapped when much more vigorous gas evolution occurred as the temperature rose above  $10^{\circ}\text{C}$ . Eventually, a low temperature circulating bath was used to cool the reaction suspension to  $\sim 0^{\circ}\text{C}$  while the reaction mixture was stirred overnight. Excessive gas evolution was probably due to decomposition of residual  $\text{LiGaH}_4$  in solution. The suspension color turned from white to dark grey as the reaction warmed up.

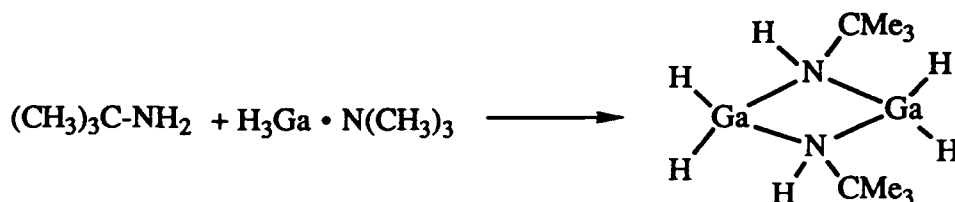
The grey suspension was filtered through a pressure filter funnel containing glass wool to trap finely divided salts. Residue left in the flask was washed with one 300 ml portion of ether and filtered. The filtrate was slightly cloudy and colorless. The grey filter cake was quite water-reactive, effervescing vigorously, though not explosively. Disposal was accomplished by wetting the salt with hexane (or toluene), followed by isopropanol, and finally total dissolution in water (Caution).

The solvent was vacuum transferred away from filtrate, leaving white solid residue behind. Removal of crude product was hampered by the fact that the solid stuck tenaciously to the bottom of the flask. The total crude product yield was 103.1g.

A sublimator was loaded with 29.8g of crude material for purification by sublimation. A yield of 14.4g of product was isolated from the first batch of 29.8g sublimed. Further sublimations gave an additional 38.9g of product from a total of 53g crude. Another 25g or so of crude material remains to be sublimed. The sublimations in general took about two days.

Proton nmr ( $C_6D_6$ ) was not illuminating: 1.67 ppm, s, 9H ( $NMe_3$ ) and a broadening in the baseline from ~4.7-6.0 ppm for the gallium hydrides. The quadrupolar effect of the gallium nucleus undoubtedly contributed to the broadening of the hydride resonances.

### Gallane:t-butylamine **3**



Trimethylamine gallane (10.2g, 0.0774 moles,) was placed in an oven dried, 500 ml, three necked flask in the drybox. Ether (100 ml, distilled from sodium benzophenone ketyl) was added and the resulting solution cooled to  $-20^{\circ}C$ . The flask was fitted with a dropping funnel to which a nitrogen sparged solution of t-butylamine (5.5g, 0.074 moles, Aldrich) was added. The amine solution was added over 80 minutes to the stirred gallane solution which was maintained at  $-20^{\circ}C$  during the addition. A white solid gradually formed during the addition and very slow gas evolution was observed. The reaction mixture was allowed to warm slowly to room temperature and stirred at room temperature overnight.

After stirring overnight an aliquot was removed, solvent evaporated, and the white solid residue examined by NMR (solid dissolved readily in  $C_6D_6$ ). Broad singlets were seen at 0.29, 0.63 and 1.64 ppm as well as residual ether.

The ether was removed from the reaction mixture by evaporation under a stream of nitrogen. The white solid residue (12g) was sublimed at  $30-40^{\circ}/50\mu m$ . (Oil bath temperature was originally  $50-60^{\circ}$  but this resulted in a pressure rise in the sublimator.) A white, slightly wet solid was collected (5.5g). NMR ( $C_6D_6$ ):  $\delta$  0.76, 1.74, 2.76 ppm. Ratio 4:1:1. Also a broad peak at 5.3ppm. The identity of this product is unclear. Reported NMR for t-butylamine gallane is 1.03, 1.04 (cis and trans isomers) and 0.85ppm (monomer). NMR signal for t-butylamine is 0.99 and for trimethylamine 2.05.



Repeat

In the drybox, trimethylamine gallane (0.142g, 0.00108 moles) and t-butylamine (0.084g, 0.0015 moles) were each dissolved in 1 ml deuterobenzene and the two solutions were combined. Some cloudiness was seen as soon as the solutions were combined. The mixture was stirred in a 5 ml vial which was vented through a 25 gauge needle. An NMR was taken after two hours. The quality of the spectrum was poor, presumably due to the cloudiness of the mixture. Two singlets were seen at  $\delta = 1.88$  ppm and 0.87 ppm as well as a broad hump at 1.46 ppm. The mixture was stirred overnight at room temperature. NMR showed peaks at  $\delta = 0.96$  ppm and 1.99 ppm. The latter value was appropriate for free trimethylamine. The mixture at this point was not homogenous – a dense oily liquid settled out when stirring was halted. The vial was removed from the box and the solvent and free amine were removed by evaporation under a stream of nitrogen. The remaining white residue was sublimed in a microsublimation apparatus at 100 $\mu$ m. Some white crystals sublimed almost immediately, without heating. The oil bath temperature was gradually raised to 85°C without any additional material appearing to sublime. The sublimed material was transferred to an NMR tube in the drybox. Addition of deuterobenzene caused gas evolution. NMR showed a singlet at  $\delta = 0.57$  ppm and a broad singlet at 1.95 ppm instead of the expected three peaks in the ratio of 9:2:1.

Repeat

In a second attempt, in the drybox trimethylamine gallane (0.485, 3.68 mmoles) was weighed into a 3-neck, 100 ml flask equipped with septa and t-butylamine (0.267g, 3.66 mmoles) was weighed into a vacuum ampoule. They were removed from the box and placed on a vacuum line. Both vessels were cooled in liquid nitrogen and evacuated. The t-butylamine was then allowed to condense onto the trimethylamine gallane and the mixture warmed to room temperature. After two hours the flask was again cooled in liquid nitrogen and the non-condensable gases pumped off. The mixture was allowed to react overnight at room temperature and this procedure repeated. The volatile condensables were then vacuum transferred into the ampoule. The flask and the ampoule were taken into the drybox and NMR samples prepared from each. The white solid in the flask was only slightly soluble in deuterobenzene. NMR showed singlets at  $\delta = 0.78$  ppm and 1.85 ppm, a broad hump at 5-6 ppm (typical of gallium hydrogens) and several smaller peaks. The volatiles consisted of a mixture of trimethylamine ( $\delta = 2.05$  ppm) and t-butylamine ( $\delta = 0.98$  ppm).

Repeat

In the dry box trimethylamine gallane (~0.01g, 0.1 mmole) was weighed into an NMR tube which was then placed on a vacuum line. After removal from the box, deuterobenzene and t-butylamine (10 $\mu$ l, 7 mg, 0.1mmole) were condensed into the tube which was then sealed under vacuum. After warming to room temperature some gas evolution was observed and the solution turned cloudy (as in 093-18). NMR spectra were taken after 20 minutes and 18 hours, respectively, at

room temperature. They were essentially the same and quite similar to the example above. Two singlets were seen at  $\delta = 1.95$  ppm and 0.93 ppm as well as a broad hump at 1.41 ppm. The tube was then heated in an 80° oil bath for 4 hours. NMR showed singlets at  $\delta = 2.02$  ppm and 0.96 ppm. There was some evidence for gallium hydrogens but the baseline was too poor to be sure.

#### Repeat

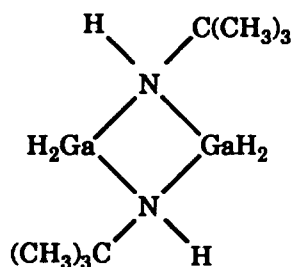
The procedure above was repeated but using a vacuum ampoule as the reaction vessel so that there would not be any septa present which might leak over an extended period of time under vacuum. Trimethylamine gallane (0.394g, 2.99 mmoles) was allowed to react with t-butylamine (0.31 ml, 0.238g, 3.25 mmoles) for 18 hours at room temperature. Volatile condensables were removed as before; 0.021g were collected which GC showed to be a 1:1 mixture of trimethylamine and t-butylamine. NMR of the off white solid residue showed singlets at  $\delta = 0.81$  ppm and 1.79 ppm, a broad singlet at  $\delta = 1.67$  ppm and a broad hump at  $\delta = 5.4$  ppm. The residue (aside from a small sample set aside - see below) was placed in a microsublimation apparatus. When the temperature of the oil bath reached 40-45°C, 35µm the solid began to melt and gas evolved rapidly. A mixture of white solid and liquid collected on the cold finger. NMR showed peaks at 0.75, 1.75 and 2.80 ppm - very similar to 093-11 but not in agreement with the literature.

#### Repeat

A 250 ml oven-dried, three-necked flask, equipped with a condenser and magnetic stirrer, was loaded with trimethylaminegallane (2.6g, 0.020 moles). Ether (60 ml, freshly distilled from sodium benzophenone ketyl) was added via cannula and the resulting solution was cooled in an ice bath while a solution of t-butylamine (1.37g, 0.0188 moles) was added over 20 minutes. A white solid gradually formed and some gas evolution was noted. The mixture was allowed to warm to room temperature and stirred at room temperature overnight. An aliquot was removed after 24 hours and an NMR was taken ( $C_6D_6$ ) and displayed singlets at 0.73, 1.71, and 2.73 ppm and a broad hump at ~5 ppm. After stirring at room temperature for 68 hours another aliquot was removed and NMR showed a similar spectrum but the peak at 1.71 ppm had decreased in size. Since this peak presumably is caused by the starting material (1.69 ppm) this was taken as a sign that the reaction was progressing slowly. An oil bath was added and the mixture was heated at reflux. The condenser was set at ~10°C so that the trimethylamine (b.p. 3°) would be driven off but the t-butylamine (b.p. 46°) and ether would be condensed. After 20 hours at reflux an additional aliquot was taken and NMR showed that the starting material was almost completely gone. After a total of 24 hours at reflux the oil bath was removed and the solvent evaporated under a stream of nitrogen. The white residue was loaded into a microsublimation apparatus and sublimed at ~50°. The pressure rose on initial heating to ~200 mm Hg but stabilized eventually at ~90 mm Hg. 0.7g of white solid was collected from the cold finger. NMR of this sample showed peaks at 0.65, 2.33, and 5.3 ppm in a ratio of 9:2:1. This is not in agreement with the reported spectrum for the product but is plausible. The areas of the peaks at 2.33 and 5.3 ppm are reversed, however, unless one assumes that the peak at 5.3 corresponds to N-H protons and the peak at 2.33

to GaH protons. In an effort to better identify this product it was resublimed and a sample sent to Galbraith for C,H,N analysis.

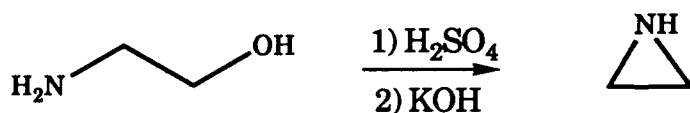
The analytical results from Galbraith showed that the product of this reaction (093-28-2, m.p. 36-44°C, NMR 093-28-B) was not the desired di-t-butylgallazane shown below.



<u>Expected</u>	<u>Found</u>
C - 32.93%	22.35%
H - 8.29%	6.53%
N - 9.60%	8.52%
Ga - 48.46%	31.42%

The identity of this compound is still unclear and the approach was abandoned.

### Synthesis of aziridine



*Journal of the Chemical Society* 1935 57, 2328

Ethanolamine (124g, 2.03 moles) was diluted with 100 ml water and to this was added sulfuric acid (206.6g, 96%, 2.02 moles) diluted with 300 ml water. This mixture was stirred and heated with a heating mantle while the water was distilled off. After several hours the mixture began to thicken and turn brown ("char"). At this point heating was discontinued and the mixture allowed to cool to a brown/white sludge. Two hundred ml of ethanol/water was added and the resulting slurry poured into a filter funnel. Chunks were broken up with a spatula. The slurry was filtered under nitrogen pressure and the off white solid washed with ethanol.

The solid was mixed in a round bottom flask equipped with a one piece distillation apparatus with a solution of 250g NaOH in 400 ml water and the mixture heated to 100°C. A clear liquid distilled

off at a head temperature of 70-80°C. ~50 ml of liquid was collected. (Much less than expected based on the above reference.) Solid KOH pellets were added to the distillate causing a separation into two phases. The top layer was removed via cannula and again dried over KOH. This crude material was distilled through a 20 cm Vigreux column. The first fraction (b.p. 50-70°, 96% by GC, primary impurity was ethanol) was collected and dried over sodium. After sitting at room temperature over sodium for several days the liquid had turned red and considerable solid was present. The sample was redistilled (b.p. 53-60°, purity = 96%) and stored at -70°. NMR 093-23-A showed a singlet at  $\delta = 1.13$  ppm ( $\text{CH}_2\text{CH}_2\text{NH}$ ) and a broad hump at  $\delta = -0.72$  ppm ( $\text{CH}_2\text{CH}_2\text{NH}$ ).

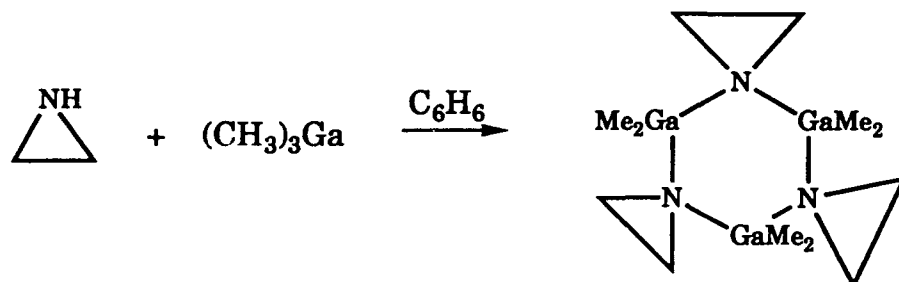
#### Attempted synthesis of aziridine:gallane



The procedure described above was also used for the reaction of aziridine (0.465g, 0.0108 moles) and trimethylamine:gallane (1.4g, 0.0106 moles). The reaction appeared to proceed more rapidly as significant amounts of white solid were formed during the addition. An aliquot taken after stirring at room temperature for 90 minutes NMR showed only a small amount of starting material still present. Unfortunately there was also no clear signal for the aziridine protons but instead a series of broad peaks in the 0.0-1.5 ppm range. The reaction mixture was stirred overnight at room temperature. Removal of solvent by evaporation under a nitrogen stream left a mixture of white solid and viscous liquid. On heating to ~45°C in a sublimator this material melted and evolved gas. A small amount of material collected on the cold finger. NMR of this material was unenlightening, again showing a number of broad peaks in the 0.0-1.5 region.

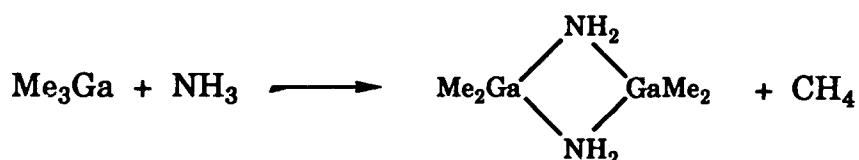
The above procedure was repeated, with the modification that the reaction mixture was refluxed overnight. NMR again showed many broad peaks in the 0.0-2.0 region. We believe that the aziridine underwent polymerization during the reaction.

### Synthesis of aziridine:trimethylgallium adduct



In the drybox a solution of aziridine (0.56g, 0.013 moles) in benzene (5 ml) was added to a solution of trimethylgallium (1.7g, 0.015 moles) in benzene (15 ml). A very slight evolution of gas was observed. After stirring overnight at room temperature a GC/MS of the solution showed only methane and benzene. The benzene was removed in vacuo leaving a clear liquid (NMR 093-35-A) which was heated under nitrogen at 140° for 2 hours. The white solid which formed (NMR 093-35-B, C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm; 1.37,s,4H; -0.53,s,6H) was sublimed at 70°C/0.90 mm (1.1g recovered, 0.0078 moles, 60% yield, m.p. 168-184°, lit. m.p. 183-185°C).

### Synthesis of dimethylgallium amide



Anhydrous ammonia was bubbled through a solution of trimethylgallium (7.1g, 0.062 moles, Texas Alkyls electronic grade) in benzene at 0-5°C. After 3 hours the ammonia was turned off and the solution was refluxed for two hours. Removal of the benzene in vacuo left a powdery white solid which was sublimed at 50°/0.09mm. Yield: 1.8g, 0.015 moles, 25% yield. NMR 093-39-B, C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm; -0.41,s. The NH protons were not seen in the NMR. GC/MS confirmed the structure shown  $m/z = 219/217/215$  ( $M^+ - CH_3$ ),  $202/200/198$  ( $M^+ - CH_3NH_3$ ),  $101/99$  ( $CH_3Ga^+$ ).

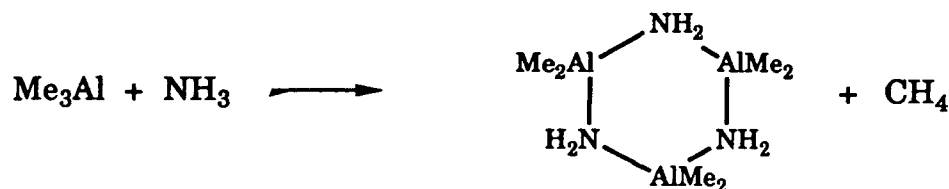
### Pyrolysis of dimethylgallium amide

The solid dimethylgallium amide was pyrolyzed at 500°C/1 torr in a simple flow pyrolysis system. Bubbler temperature was ~70°C with a flow of 15 sccm He resulting in 0.2 g of (Me<sub>2</sub>GaNH<sub>2</sub>)<sub>2</sub> passing through the hot tube in 2 hours. A small amount of solid was observed in the trap,

presumably unreacted starting material. The tube contained a yellow/tan deposit. EDX showed substantial amounts of Ga and small amounts of nitrogen but Raman spectroscopy showed no characteristic GaN peak.

The solid dimethylgallium amide was pyrolyzed using the same system but without any carrier gas. This was much less successful as the majority of the sample remained in the bubbler even after several hours at 80°/0.03 torr. The volatile material from the trap was vacuum transferred to an ampoule and examined by GC/MS. Some methane was detected but it was not possible to determine if ethylene was present. There was a slight amount of blue/black deposit in the tube which EDX showed to contain Ga but very little nitrogen. When the pyrolysis equipment is available this experiment will be repeated with a carrier gas so that a more substantial deposit can be examined and (hopefully) enough volatiles can be collected to determine whether or not ethylene is being produced.

### Synthesis of dimethylaluminum amide



A solution of trimethylaluminum (1.2g, 0.017 moles) in 50 ml pentane was prepared in the glove box. After removal from the box the solution was cooled in an ice bath and anhydrous ammonia was bubbled through the solution. A white solid formed in the solution quite quickly but then dissolved. After 2.5 hours the ammonia was turned off and the pentane was evaporated under a stream of nitrogen. The white solid which remained showed two signals in the NMR (093-45-A), at 0.16 and -0.60 ppm in a ratio of 1:5. A GC/MS of the NMR sample showed only solvent.

The sample was heated in a 70° oil bath under nitrogen. After ~10 minutes the sample melted and began to evolve gas. Gas evolution became quite vigorous and the oil bath was removed. Despite this gas evolution continued to be very rapid and the septum cap was blown off. A tan powder remained in the bottom of the flask, which was not soluble in deuteriochloroform. An EDX analysis will be performed on this sample.

The above reaction was repeated. The white solid was sublimed at 25°/0.1 mm. NMR of the sublimed material was but the ratio of the signals was 1:2.5. A small amount of the sample (~5 mg) was dissolved in deuterobenzene, sealed in an NMR tube and heated at 40°. After 15 hours new signals were seen in the NMR which appear to indicate elimination of methane and formation of new  $\text{AlCH}_3$  and  $\text{NH}_2$  protons.

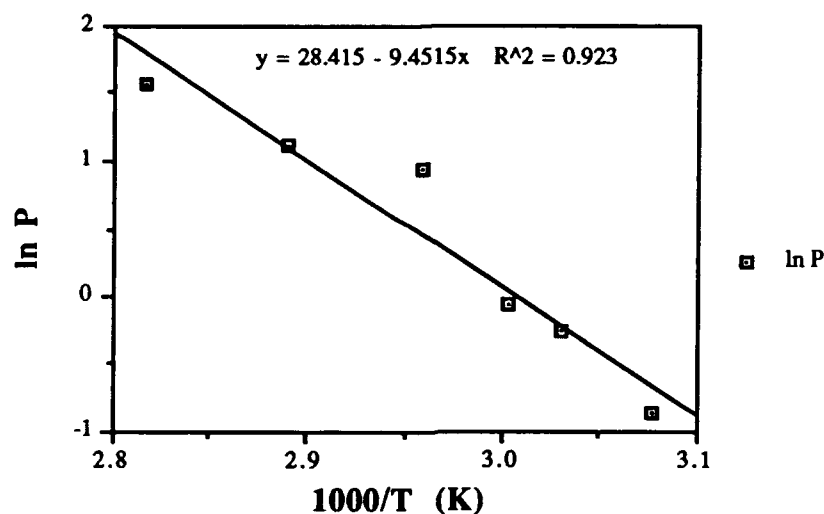
The sublimed trimethylaluminum:ammonia complex (white solid, 2.0g, 0.0225 moles) was slurried in hexane and warmed in a 40-45° oil bath. Gas evolution began almost immediately upon heating. A grey-tan solid began to form after 15-20 minutes. After 1 hour gas evolution had ceased. The mixture was refluxed overnight. Upon cooling white crystals appeared. The solution was cooled in a dry ice/IPA bath and the supernatant liquid removed via cannula. The crystals were washed with cold hexane (2 X 10 ml), dried in vacuo and sublimed at 50°C/0.1 torr. 1.1g (0.0050 moles, 67% yield) of white crystals were recovered. NMR 093-48-A ( $C_6D_6$ )  $\delta$  (ppm): -0.27, s, 6H,  $NH_2$ ; -0.78, s, 18H,  $AlCH_3$ . A small impurity peak was also seen at ~1.4 ppm.

### Note

Although the trimethylamine:gallane which had been used for the attempted syntheses of  $(RR'NGaH_2)_x$  showed little evidence of decomposition (slightly off white color, no pressure buildup in the bottle, NMR agrees with that reported by W. Kosar) it was resublimed in order to see if any non-volatile material was present. Sublimation at 25-30°C/90 $\mu$  gave 10 grams of white solid and 1 gram of unsublimed residue. The residue was not air reactive – gallium oxide? The synthesis of the aziridinyl gallane complex was attempted again using this resublimed material and the literature procedure (*JCS* (1972), 326). The crude product was only slightly soluble in  $C_6D_6$  and gave an NMR with several peaks, one of which may correspond to the correct material ( $\delta$  = 1.51 ppm, lit = 1.54). Attempted sublimation of this material at 60°/75 $\mu$  resulted in no sublimed material.

## d.2 REAGENT CHARACTERIZATION

Vapor pressure measurements were performed on  $[(CH_3)_2GaNH_2]_2$  using a vapor pressure apparatus equipped with a MKS Baratron gauge and oven thermostatically controlled to  $0.1^\circ C$ .



Because of fluctuations in the instrument, multiple measurements were required at each temperature in order to obtain reasonably reliable data.

Extrapolation of the vapor pressure data above to room temperature shows that it is not reasonable to expect to grow films from this reagent at atmospheric pressure without a heated source and transfer lines:

$$VP \text{ at } 20^\circ C = e^{(28.415 - 9.4515(1000/293))} = 0.0214 \text{ torr}$$

$$\begin{aligned} \text{Mass transported} &= (VP / P_{\text{system}}) \times (\text{carrier gas flow} \times \text{time} / 22.4) \times MW \\ &= (0.021/760) \times (0.1 \text{ slpm} \times 120 \text{ min} / 22.4) \times 230 = 0.0035 \text{ grams} \end{aligned}$$

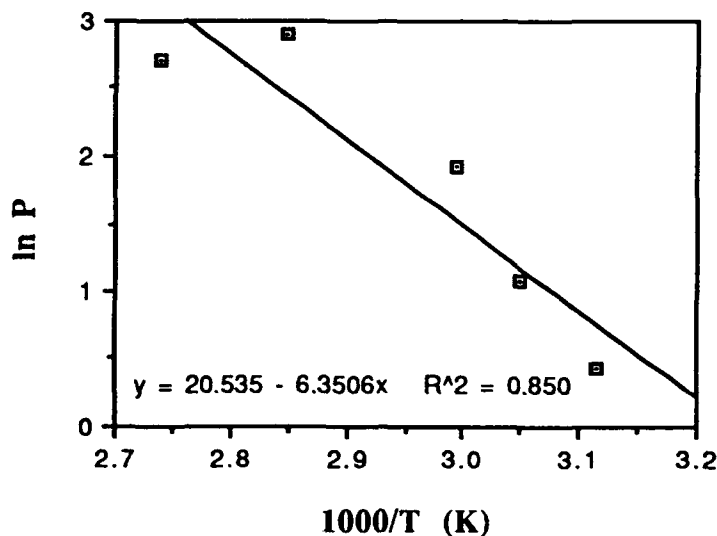
However, at reduced pressure, assuming a pressure at the bubbler of 5 torr:

$$\text{Mass transported} = (0.021/5) \times (0.1 \text{ slpm} \times 120 \text{ min} / 22.4) \times 230 = 0.53 \text{ grams}$$

Of course the assumption that this data can be extrapolated to room temperature may not be valid, but it appears that it is worth trying.



Vapor pressure measurements were carried out on  $[(\text{CH}_3)_2\text{AlNH}_2]_3$ :



Extrapolating to 20°C:  $\text{VP at } 20^\circ\text{C} = e^{(20.535 - 6.3506(1000/293))} = 0.32 \text{ torr}$

The mass transported in a two hour growth run will therefore be:

$$\begin{aligned} \text{Mass transported} &= (\text{VP} / P_{\text{system}}) \times (\text{carrier gas flow} \times \text{time} / 22.4) \times \text{MW} \\ &= (0.32/760) \times (0.1 \text{ slpm} \times 120 \text{ min} / 22.4) \times 230 = 0.048 \text{ grams} \end{aligned}$$

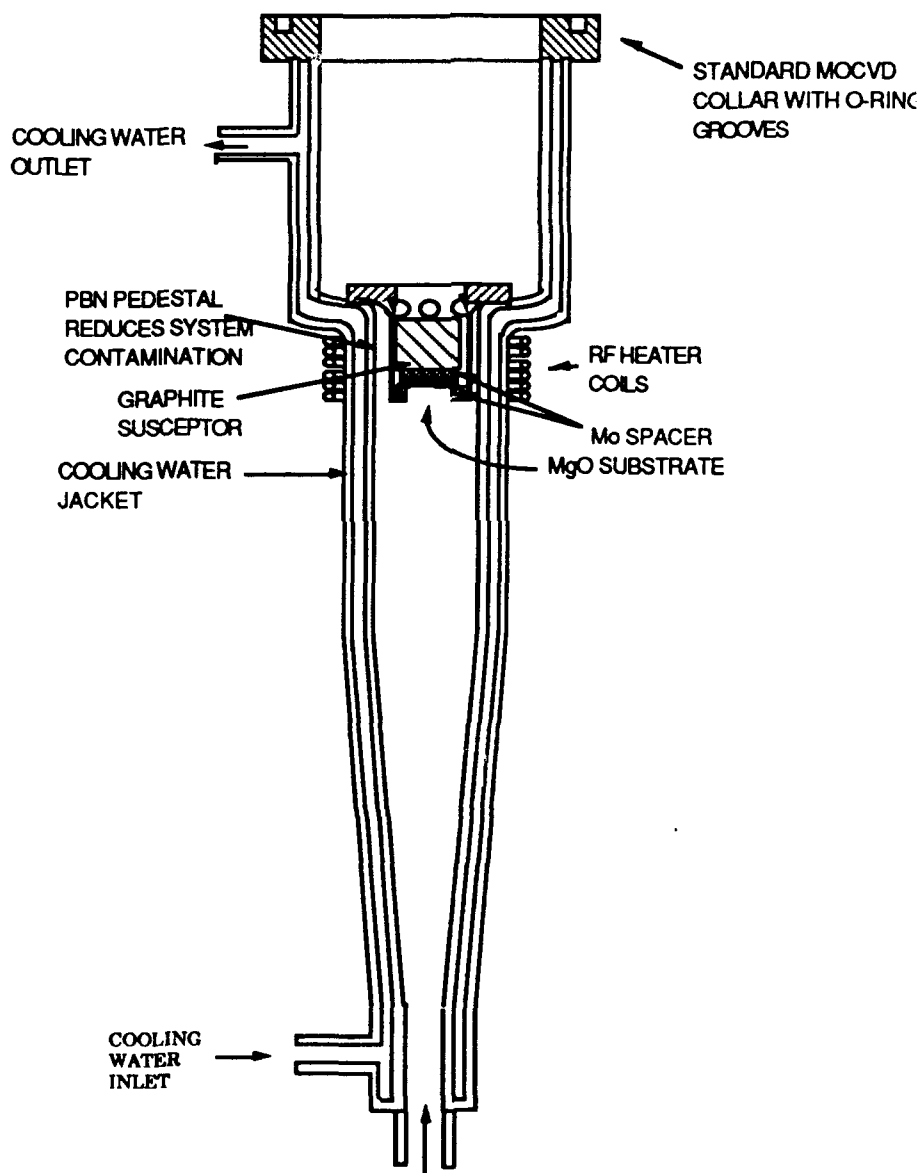
In addition to the extrapolation to room temperature, a potential problem with this calculation is the question of whether the gas phase species is a trimer or not.

C,H analyses were received back from Galbraith for three compounds:  $(\text{H}_2\text{NGaMe}_2)_2$ ,  $(\text{H}_2\text{NAlMe}_2)_3$  and  $(\text{CH}_2\text{CH}_2\text{NGaMe}_2)_3$ . The analyses were correct for the first two compounds but were low on both C and H for the aziridine compound.

### d.3 FILM GROWTH

#### Low pressure chemical vapor deposition

Since the aluminum compounds were easier to prepare and were thermally more stable than the analogous gallium compounds, film growth was attempted in a low pressure inverted vertical reactor using  $[(\text{CH}_3)_2\text{AlNH}_2]_3$  and  $[(\text{CH}_3)_3\text{N:AlH}_3]$ . The reactor is shown schematically below:



Group III Organometallic + Nitrogen source +  $\text{H}_2$

**Inverted vertical reactor used in the attempted growth of AlN thin films by low pressure chemical vapor deposition.**

A polished 10mm x 10mm MgO crystal was rinsed in warm trichloroethane, methanol, and deionized water, then blown dry and loaded onto a graphite susceptor which was placed in the reactor. A bubbler containing 1.1g of  $[(\text{CH}_3)_2\text{AlNH}_2]_3$  was connected to the gas delivery manifold. The sample was heated under a flow of 1.67 slpm of hydrogen and the flow was then turned down to 0.12 slpm (flow was reduced in order to lower pressure in the system and maximize transport of relatively involatile source reagent). Other parameters:

Source T:	20°C
Susceptor T:	550°C
Source flow:	80 sccm $\text{H}_2$
Growth time:	105 minutes
Pressure:	0.5-1.0 torr

The pressure at the bubbler could not be measured. One additional problem was that the bypass line could only be operated at atmospheric pressure whereas the reactor was at reduced pressure. Therefore when the reagent gas stream is transferred from the bypass line into the reactor there is a large drop in pressure which may lead to solid material being blown into the lines.

No film was observed on the substrate either visually or by SEM/EDX. The bubbler had a mass loss of 0.120 grams.

An additional attempt was made to grow an AlN film on an MgO substrate using hydrazine and trimethylamine:alane. Parameters:

Source T (both):	20°C
Susceptor T:	500°C
Source flow (both):	80 sccm $\text{H}_2$
Growth time:	90 minutes
Pressure:	760 torr

Once again, no film was observed either visually or by SEM/EDX. It was thought that reaction of the source reagents might be occurring in the lines to form the relatively involatile hydrazine:alane adduct. Disassembly of the system revealed that there was a white powder in the lines. The relevant portions of the system were ultrasounded in methanol in an attempt to remove this material.

The system was then modified to allow for independent transport of the hydrazine and trimethylamine:alane to the reactor.

Two growth runs were done using trimethylamine:alane and hydrazine as source reagents. The gas handling system was modified so that the alane and hydrazine travelled independently to the

reactor. The diluent flow and alane entered through the central tube and the hydrazine entered through the side tube (see diagram). Parameters:

H <sub>2</sub> diluent flow:	2400 sccm
Me <sub>3</sub> N:AlH <sub>3</sub> flow:	500 sccm
H <sub>2</sub> NNH <sub>2</sub> flow:	50 sccm
Substrate T:	500 °C
Run time:	42 min

Source reagent temperatures were not controlled due to a lack of functioning chillers. A gray deposit was observed on the substrate and on the upper walls of the reactor tube. A white deposit was observed on the lower walls of the reactor tube. SEM/EDX of the substrate showed nodular growth – primarily aluminum but also containing some nitrogen and chlorine.

The second run used similar growth parameters but the alane and diluent flow were brought in through the side tube and the hydrazine through the center tube which was also lowered to approximately 6" from the substrate. Considerable white powder was observed on one side of the reactor tube but no deposit was observed on the wafer. Hydrodynamics are clearly a problem – alane/diluent flow needs to be made more uniform.

Two more growth runs were done using trimethylamine:alane and hydrazine as source reagents with a further modified growth system. The alane and diluent flow was split and brought in on both sides at the bottom of the reactor (see diagram above) and the hydrazine flow was brought in through the center axial tube.

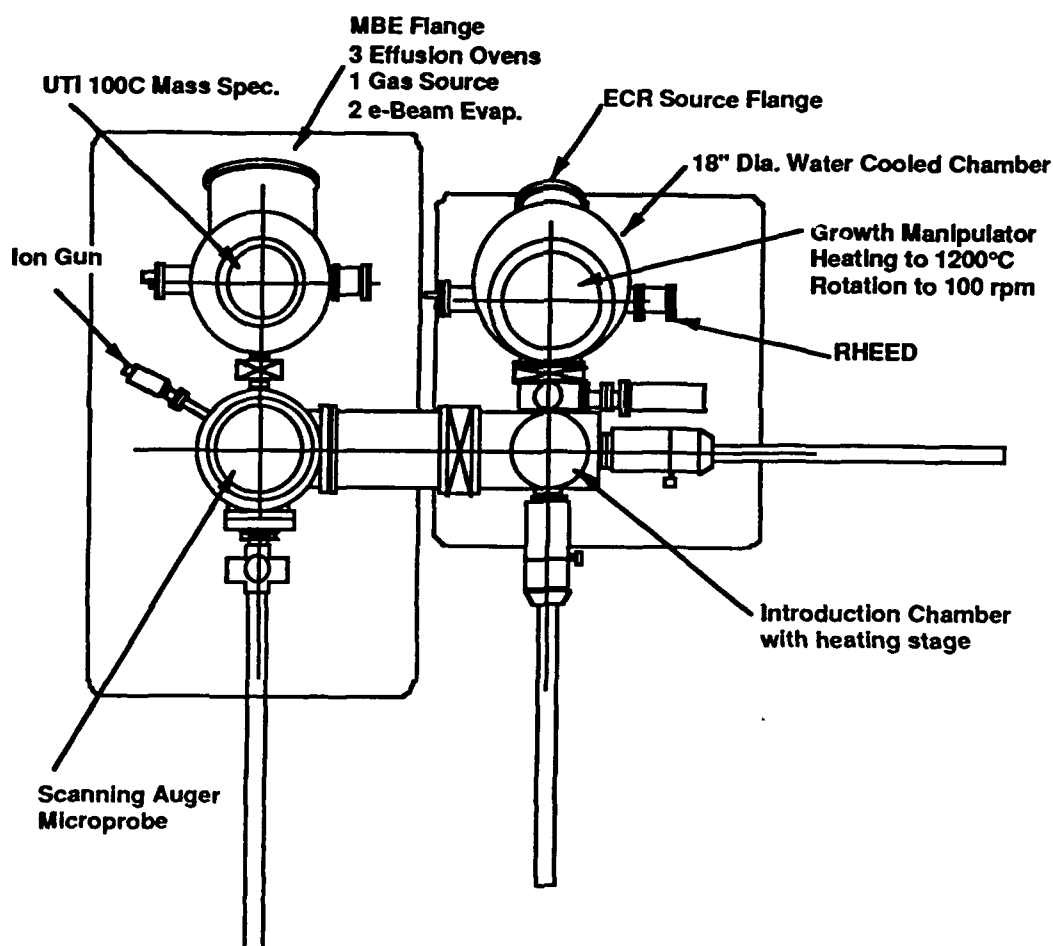
H <sub>2</sub> diluent flow:	2500 sccm
Me <sub>3</sub> N:AlH <sub>3</sub> flow:	400 sccm
H <sub>2</sub> NNH <sub>2</sub> flow:	80 sccm
Substrate T:	500°C
Run time:	60 min

Source reagent temperatures were not controlled due to a lack of functioning chillers. A white deposit was observed around and above the susceptor but there was no evidence of growth on the substrate. SEM/EDX showed particulates on the surface which contained aluminum but there was no evidence of nitrogen.

The second run used similar growth parameters but the hydrazine and alane were mixed at the very bottom of the reactor. Again a white powder was observed on the walls of the reactor but no growth was seen on the substrate.

## Chemical beam epitaxial growth of GaN

The growth experiments were carried out in an MBE system coupled to an analysis chamber equipped with Auger electron spectroscopy (AES). The base pressure of the system was  $3 \times 10^{-10}$  torr. The reactor is shown schematically below:



Schematic of the CBE growth and analysis chamber

Substrates were MgO (100). Before loading the substrate into the MBE system, the substrate surface was rinsed with isopropanol, methanol, and then dried in argon. Substrate heating was accomplished by passing current through a rhodium filament placed directly beneath the substrate. The temperature was monitored with a thermocouple placed between the film and the edge of a stainless steel clip. Uncertainty exists in the absolute measurement of the substrate temperature but the process proved to be reproducible run-to-run. Results for each source combination are given below.

### **Dimethylgallium amide**

The dimethylgallium amide (DMGA) 1-Ga was introduced into the system via a heated manifold and a variable leak valve. The bubbler containing 1-Ga was heated to 90°C and the transport lines were heated to 150°C to prevent condensation of the source.

The MgO substrate was exposed to greater than 10<sup>5</sup>L of DMGA between 250°C and 650°C. At temperatures less than 300°C, the Mg and O remained the dominant feature in the AES. We believe that the temperature was too low to initiate decomposition.

At temperatures between 350°C and 550°C, the Auger C KLL to Ga LMM line intensity ranged between 1.8 and 2.8. No obvious correlation between the C:Ga ratio was observed. The N:Ga line intensity ratio was 2.8 for the 350°C and 450°C depositions, corresponding to a 1:1 atomic ratio. At 550°C the Auger line intensity ratio dropped to ~1 and at 650°C no film was deposited.

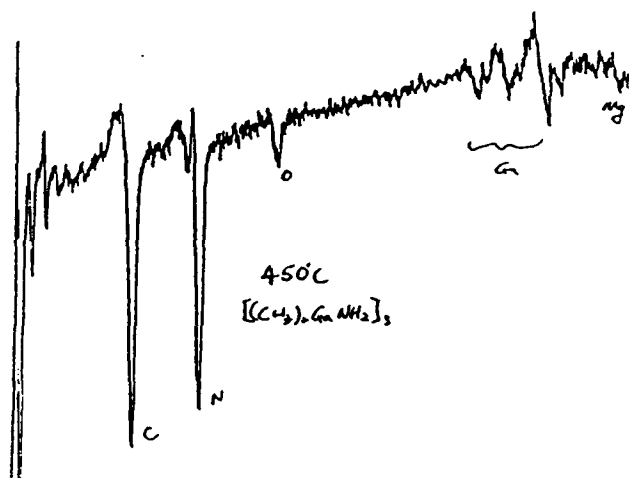
### **Dimethylgallium amide and NH<sub>3</sub>**

Under a fixed ratio of dimethylgallium amide to ammonia of 1:100, MgO substrates were exposed to 10<sup>4</sup>L of dimethylgallium amide at temperatures between 350°C and 550°C. Below 350°C the Auger signal was dominated by MgO. At 450°C, the N:Ga Auger line intensity is ~3, corresponding to a 1:1 atomic ratio. The C:Ga line intensity dropped to ~0.65, a dramatic reduction in the amount of carbon compared to that observed when only the dimethylgallium amide was used. At 550°C the N:Ga line intensity remained high but the C:Ga ratio also climbed dramatically.

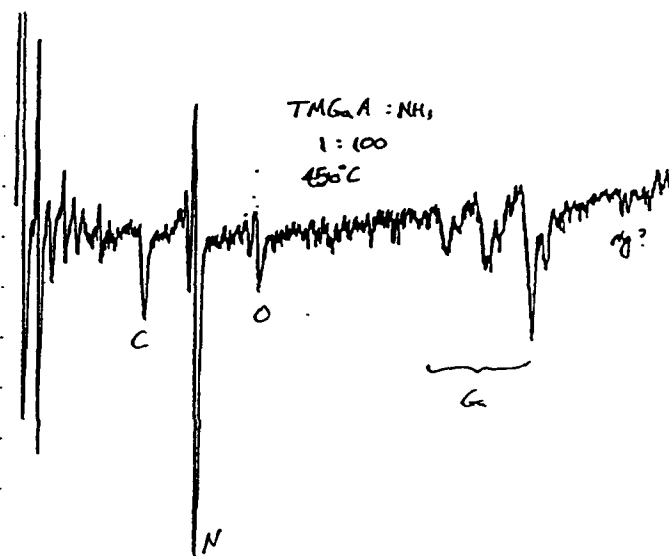
### **Trimethylgallium and NH<sub>3</sub>**

Growth of GaN from trimethylgallium and ammonia was examined in order to determine if the presence of a preformed C-N bond was important. Even after long exposures of trimethylgallium (up to 10<sup>6</sup>L) and ammonia, only poor coverage of the surface was obtained. The C:Ga remained high. (see Figure on next page)

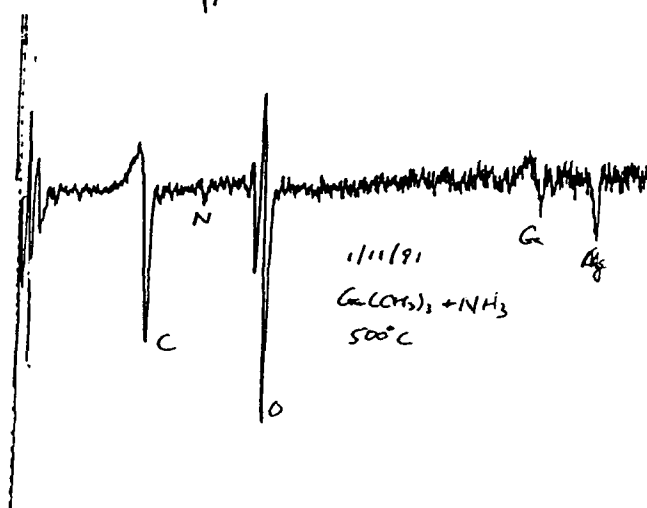
A.



B.



C.



Auger spectra of films deposited by chemical beam epitaxy with dimethylgallium amide (A), dimethylgallium amide and ammonia (B) and trimethylgallium and ammonia (C)

#### **e. TECHNICAL FEASIBILITY AND IMPLICATION FOR FURTHER RESEARCH**

We have shown that growth of gallium and nitrogen containing films can be grown from organometallic compounds and ammonia under chemical beam epitaxy conditions. The ratio of carbon to gallium is dramatically reduced if the a) the Ga-N bond is preformed and b) ammonia is added to gas stream.

We have recently discovered that the starting material for the Ga-H based compounds was contaminated and may have led to our inability to prepare samples of 3 and 4.

Further research should concentrate on the optimization of the growth conditions of GaN from the dimethylgallium amide and ammonia, as well as re-examine the preparation of the gallane complexes from higher quality starting material.

#### **f. SIGNIFICANT HARDWARE DEVELOPMENT**

None.



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